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Original Article

RESEARCH OF THE PROCESS FOR THERMAL DEHYDRATION OF ORTHOPHOSPHATE IS SODIUM PHOSPHATE FROM CENTRAL KYZYLKUM

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ABSTRACT

This research is on the process for high-temperature dehydration of sodium orthophosphates with the ratio $Na_2O:P_2O_5$ = 0.73 in pH = 6.3. Temperature parameters for the formation of sodium tripolyphosphates form I and form II using physico-chemical methods are established. It shows the synthesis possibility of sodium tripolyphosphate in the set form.

Dried samples of a mixture of 1 mole of dihydrogen phosphate and 2 moles of sodium hydrogen phosphate was prepared and heated for 1 hour at temperatures of 360 to 560°C. During dehydration at temperature 360°C, only phase II is formed, which is characterized by intense peaks 4,6911, 2,6898, 4,5091, 2,6215, 2,5843, 4,4572, 4,4181, 3,0612 Å. Similar peaks are characteristic in the form I of sodium tripolyphosphates. Difference in the x-ray peaks are 4,6911 and 2,6898 Å. Form II has a maximum value of the peaks at 4,6911 Å, and form I has a maximum value at 2,6902 Å. X-ray of sodium tripolyphosphates form II and form I are almost the same.

In IR spectrum $Na_5P_3O_{10}$ four groups of absorption bands in the intervals 570-750, 890-1015, 1095-1215 and 1255-1285 cm^{-1} were identified, indicating the long-chain structure of the anion compound. Structure $Na_5P_3O_{10}$ consists of the continuous P–O–P chains arranged along the cleavage of the fiber, in which each phosphorus atom is in tetrahedral coordination.

On derivatograms there are many exo and endoeffective. Endoeffect at 163 and 267°C corresponds to the formation of $Na_2H_2P_2O_7$. At 163°C weight loss makes 12.00%, while 267°C 17,15%. Theoretical losses are 11.96% and 17.1%.

Thermo chemical transformations at temperature 300-400°C are accompanied by removal of 0.5 mol water and formation $Na_5P_3O_{10}$ II. At temperature 450-620°C, reactions transform the form II into form I. At temperature above 620°C sodium hexametaphosphates of amorphous structure is formed.

KEYWORDS: Dehydrated Sodium Phosphates, The Forms Ii & I, Pyro-, Metaphosphates, Chain Structures, Endo- & Exothermic Effects

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INTRODUCTION

Sodium tripolyphosphate is used in many industries due to its specific properties. However, the main consumers are manufactures of synthetic washing- liquids, where sodium tripolyphosphate is used for water softening [1–3]. Sodium tripolyphosphate is an active filler that provides the best characteristics and the minimum influence on environment. For manufacturing of washing-up liquids sodium tripolyphosphate with the required specific volume density, granulometric composition, crystal phase (form I and II) and moisture content [4–6] is used.

A large part of the sodium phosphates is used for the preparation of boiler water, and for cleaning boilers. Their addition to feeding water prevents scaling in coppers. [7–8]. They are also used as lubricant-cooling liquids in mechanical processing of metals [9–11].

An amount of 9.0-11.6% sodium tripolyphosphate is used in concrete to prevent its shrinkage during rolling [17–20]. Its addition to the composition of silicate adhesives, an amount of 3, 6-5, 0% contributes to the hardening of the composition and this eliminates warping of the glued products, which increases the durability and protective properties [21–22]. When the sulfate soap obtained from ferrous metal waste, is added to sodium tripolyphosphate it increases the yield of the product [23–26].

The main property that determines the use of sodium polyphosphates are cheapness, economic safety and biodegradability.

Thus, the development of technology for obtaining sodium tripolyphosphates with specified compositions and predicted physical - chemical properties of phosphorites from Central Kyzylkum is an urgent need in modern chemical science and production work.

EXPERIMENTAL PART

Sodium tripolyphosphate is obtained by the extraction of phosphoric acid on the basis of phosphorites Central Kyzylkum through its clearing from fluorine, sulfates, and deep clearing of fluorine, calcium and one-and-a-half oxides by neutralization of sodium carbonate to pH 4.5 and magnesium ammonium gas to pH 6.3-6.5. After this branch of magnesium ammonium phosphate deposits range from pH 8.0-8.5. The cleared solution has pH 6.3 and the ratio $Na_2O:P_2O_5$ is equal to 0.73, which corresponds to a mixture of 1 mole of dihydrophosphate and 2 moles hydrophosphate sodium. The solution is evaporated to a wet state and dried at temperature 100-110°C in a constant weight. The dried product is calcinated in a muffle furnace to obtain sodium tripolyphosphates at a temperature of 360°C and 560°C for 1 hour.

Identification of specimens is carried out on the basis of diffraction patterns, which were made on the apparatus XRD-6100 (Shimadzu, Japan), controlled by a computer. CuK_α- radiation (β-filter, Ni, 1.54178 tube current and voltage mode 30 mA, 30 kV) and a constant speed of rotation of the detector 4 deg/min with a step of 0.02 deg were used. (ω/2θ- coupling), and the scan angle was changed from 4 to 80^o.

The spectra of the samples that were taken using the IR-Fourier spectrometer IRTracer-100 were completed with the prefix single NIP c prism diamond/ZnSe MIRacle 10. It is designed for the analysis of solid, liquid, paste-like, gel-like and hard-to-process substances in the scanning range of: 4600–600 cm^{-1}. The sample in the form of powder is placed on a diamond window in the center of the console.

The thermograms were registered on a derivatograph Q-1500 D (Hungary), the system Paulik, in air atmosphere in the temperature range of 20 to 1000°C when the heating rate of the sample is equal to 0.17 k / s.

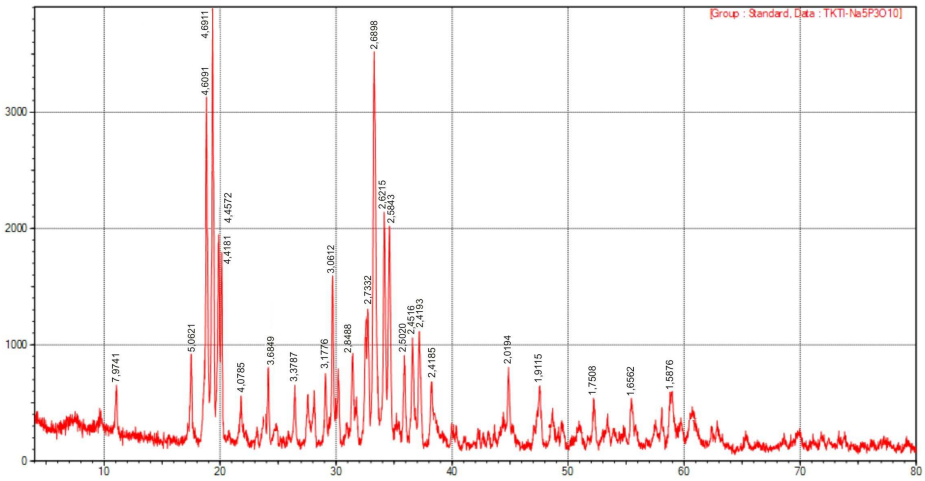
RESULTS AND DISCUSSIONS

A mixture of sodium orthophosphate hasd ratio $Na_2O:P_2O_5$ = 0.73 and have been obtained from cleared solutions with pH of 6.3. Figure 1 shows x-ray patterns of samples sodium tripolyphosphate calcined at 360 and 560^{o}C. During dehydration at temperature 360°C only phase II is formed, which is characterized by intense peaks 4,6911, 2,6898,

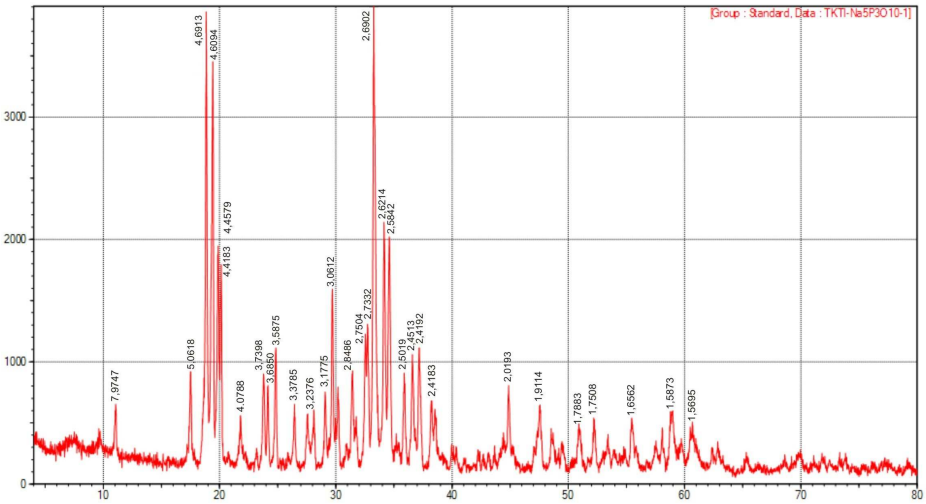
4,5091, 2,6215, 2,5843, 4,4572, 4,4181, 3,0612 Å. Similar peaks are characteristic and for the form I of sodium tripolyphosphates. The difference in the x-ray peaks are 4,6911 and 2,6898 Å. Form II has a maximum value of the peaks at 4,6911 Å, form I has a maximum value at 2,6902 Å. X-ray of sodium tripolyphosphates the form II and the form I are practically identical.

IR - spectra of the samples calcinated at 360 and 560°C are shown in figure 2 (a and b).

Vibrational absorption spectra of compounds is characterized by the features inherent in the IR spectra of polyphosphates. In the IR spectrum of $Na_5P_3O_{10}$, four groups of absorption bands can be distinguished in the intervals of 570–750, 890–1015, 1095–1215 and 1255–1285 cm^{-1}, indicating the long-chain structure of the anion compound. In the field of asymmetric stretching vibrations of PO_2 groups is highlighted and the intensive band at 1275–1285 cm^{-1}, is shown with a shoulder, and in the frequency of symmetrical oscillation of the POP groups is dominated by a band at 1095–1215 cm^{-1}. Displacement of position of absorption bands maxima of PO_2 and POP groups in the long-wave region, as well as the change in the intensity absorption bands reflect the influence of natural citations and the degree polymerization the anion.

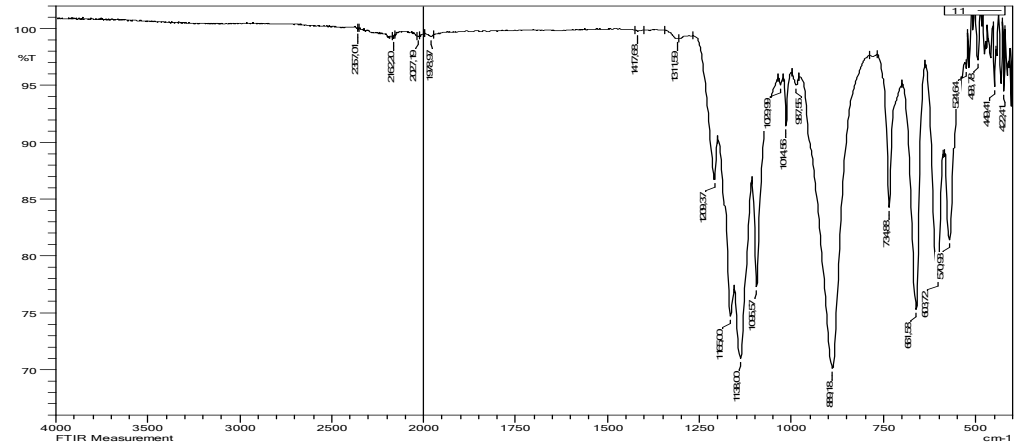


(a)

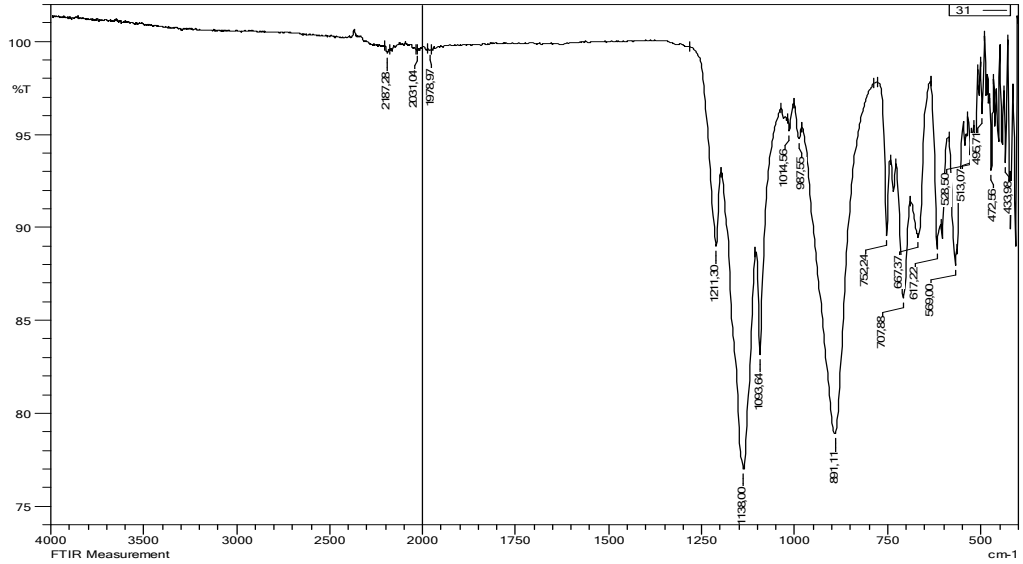


(b)

Figure 1: X-Ray of Sodium Tripolyphosphate Obtained at a Temperature of 360°C – a and 560°C - b.



(a)



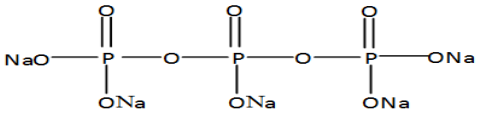
(b)

Figure 2: The IR Spectra of Sodium Tripolyphosphate, Obtained at A Temperature of 360°C - a and 560°C - b.

The IR-spectrum of the isolated compound is inherent in chained polyphosphates with four tetrahedrons PO_4 in the identity period. This conclusion is confirmed by significantly widened bands of asymmetric and symmetric oscillations of PO_2 and POP groups. Thus, the IR-spectrum of the connection can be related to the chained structures as it is in the frequency range of asymmetric valence vibrations of the ν_{as} chains P-O-P. That is the intensity of the lines is very high and its boundary from the low frequencies reaches a value of 910 cm^{-1}.

Two strips in the field of 570-660 cm^{-1} characterize the fluctuations of all chain POP as uniform formation. Analysis in the IR spectrum of the compound leads to the conclusion that the repeated structural link in the anion of the compound is a group in which the tetrahedral phosphorus atom is coordinated by four oxygen atoms.

By results of IR spectroscopy, one can make a judgment about the process of complexation in the $Na_5P_3O_{10}$ system. In phosphate melts chain, the molecular ions of condensed phosphates is exchanged between the structural units at the expense of rupture and formation of communication – P – O – P –. At the same time, the equilibrium of the restructuring process is such that in the melt of the metaphosphate composition there are mainly middle groups of PO_4. In the case of complete ionization, each of these groups has one negative charge.



Thus, structure $Na_5P_3O_{10}$ consists of continuous chains P – O – P, arranged along the cleavage of the fiber, in which each phosphorus atom is in tetrahedral coordination.

Figure 3 shows a derivatogram of a mixture of sodium phosphates with the ratio $Na_2O:P_2O_5$ = 0.73 dried at a temperature of 100-110°C. On derivatograms there are many exo and endoeffective. Endoeffect at temperatures below 150°C corresponds to removal of crystallization of waters. Endoeffect at 163 and 267°C correspond to formation $Na_2H_2P_2O_7$. At 163°C weight loss makes 12,00 %, and at 267°C 17 to 15 %. Theoretical losses are 11.96% and 17.1%, respectively, which indicates the course of reactions

$$2NaH_2PO_4 \xrightarrow[-H_2O]{160-240\ ^\circ C} Na_2H_2P_2O_7$$

$$2Na_2HPO_4 \xrightarrow[-H_2O]{250-270\ ^\circ C} Na_4P_2O_7$$

Thermo chemical transformations at temperature 300-400°C are accompanied by removal of 0.5 mol waters and formation $Na_5P_3O_{10}$ II. At temperature 450-620°C reactions transform the form II into form I. At a temperature above 620°C sodium hexametaphosphates which are amorphous structure are formed. The exothermic effect at 561°C is not accompanied by mass loss and the endothermic effects indicate polymorphic changes, which can be attributed to the transition of the form II in the form I.

These processes can be characterized course following reactions:

$$2Na_4P_2O_7 + Na_2H_2P_2O_7 \xrightarrow[-H_2O]{300-400\ ^\circ C} 2Na_5P_3O_{10}\,(II)$$

$$Na_5P_3O_{10}\,(II) \xrightarrow{300-400\ ^\circ C} Na_5P_3O_{10}\,(I)$$

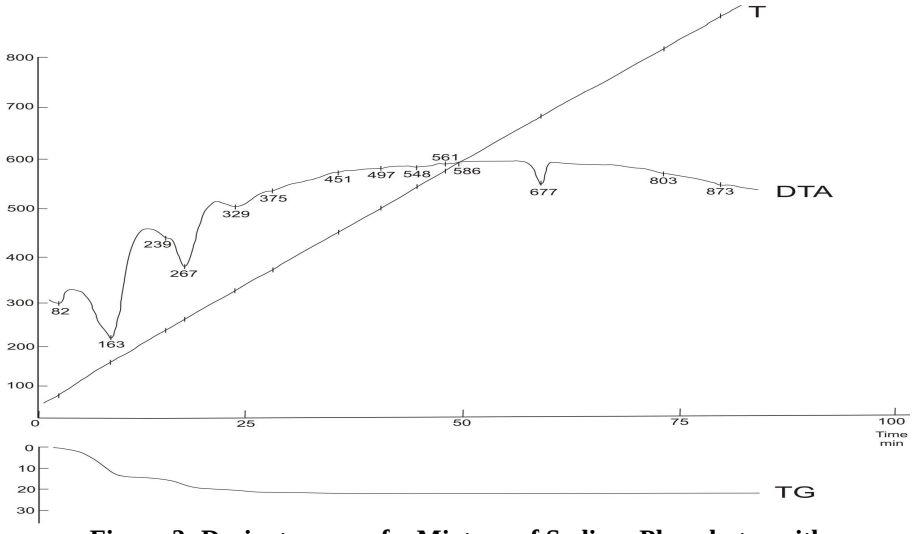


Figure 3: Derivatogram of a Mixture of Sodium Phosphates with Ratio Na2O:P2O5 = 0.73 Dried at a Temperature of 100-110oc.

CONCLUSIONS

Thus, the physic-chemical researches of a mixture of sodium orthophosphates from 2 mole Na_2HPO_4 and 1 mole NaH_2PO_4 at the ratio $Na_2O:P_2O_5$ = 0.73, is obtained at pH = 6.3 which is shown as a result of heat treatment of $Na_2H_2P_2O_7$. The formation occur at temperatures close to 240°C. $Na_4P_2O_7$ occurs at temperatures 270°C and $Na_5P_3O_{10}$ form II is obtained at temperatures to 400°C and $Na_5P_3O_{10}$ form I is obtained at temperatures to 620°C. At temperature above 620°C $Na_6P_6O_{18}$ is formed. The obtained results are confirmed using x-ray phase and IR - spectroscopy by analysis methods.

The obtained results indicate the possibility of the direct synthesis of sodium tripolyphosphates with the necessary operational properties.

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